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Betty Pang
Ames High School

Kenneth E. Windom
Iowa State Universtiy

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Nuclear Waste Into Glass: Viscosities of Molten Analogs of Radioactive Waste Disposal Media

BETTY PANG
Ames High School, Ames, Iowa 50010

KENNETH E. WINDOM
Department of Geological and Atmospheric Sciences
Iowa State University, Ames, Iowa 50011

Disposal of high-level radioactive wastes involves vitrification of a mixture of waste products and borosilicate glass frit. Monitoring the composition of the mixture is critical to the control of the vitrification process, but is difficult because of the high levels or radioactive components in the mixture. Synthetic non-radioactive analogs of the products from nuclear reprocessing have been prepared and their viscosities measured over a wide range of temperature appropriate to those of the vitrification process. Preliminary results indicate that viscosity is a linear function of composition, under isothermal conditions, for a limited compositional range that encompasses the proportions of waste products and borosilicate frit determined to be optimum for disposal of wastes at the Defense Waste Processing Facility in South Carolina. These results support the concept that physical properties of the molten waste mixtures can be used to monitor composition.

INDEX DESCRIPTORS: radioactive wastes, vitrification, viscosity, high-temperature processes

Hundreds of millions of liters of high-level radioactive liquid waste have been generated from reprocessing of nuclear fuel from commercial power plants and from national defense operations. Disposal of this large amount of hazardous material is a major societal problem, both because of the quantities involved and because these materials will continue to be radioactive for many human generations into the future.

Vitrification of high-level radioactive wastes is the currently preferred process for their disposal. Reprocessing of alkaline high-level liquid waste at the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) in South Carolina involves separation of the insoluble portion of the waste, known as "sludge" from the supernatant liquid. Virtually all the long-lived radionuclides are contained within the sludge. The supernatant liquid, containing the soluble portion of the waste, is chemically treated with sodium tetraphenylborate to precipitate alkalis, especially radioactive cesium, from the soluble waste. The precipitated material undergoes hydrolysis to produce an alkali- and borate-rich product known as "PHA" (Plodinec, 1986). The sludge and PHA are mixed with a borosilicate frit in predetermined proportions and the mixture melted in a high-temperature furnace. The molten mixture is poured into stainless steel canisters where the melt cools to form glass. The canisters are sealed and will eventually be placed in underground storage facilities, which are located in arid environments to minimize contact of ground water with the storage materials (Chapman et al., 1986; Marshall, 1987).

Two desirable characteristics of the glass storage media are 1) they be able to contain large amounts of the radioactive waste products, to minimize the volume of materials to be stored, and 2) they be chemically stable over a long time interval to minimize release of radioactive elements to the environment. Engineers at Savannah River Technical Center (SRTC) have determined that the proportions of frit:sludge:PHA in the ratios 64:28:8 (by weight) is the nominal composition. Minor adjustments to these ratios will be made for each batch of melter feed. Blending of the waste products with the borosilicate frit to attain the optimum composition must occur prior to pouring the melt into the stainless steel canisters, given the difficulties inherent with reprocessing the material subsequent to its encasement.

One technique proposed for monitoring the composition of the melt is to measure its viscosity and density at the process temperature (Schneider, 1990). The intersection of characteristic lines representing constant values of these physical properties is unique for a given composition in simple ternary systems such as Na_2O-B_2O_3-SiO_2, and Schneider (1990) argued that this observation could be expanded to the much more complex compositions encountered in actual radioactive wastes. This paper gives results from a project designed to evaluate that proposal by measuring viscosity variations in non-radioactive

Table 1. Compositions (Weight Percent) of Analog Glass Components and Reagents Used in Their Preparation.

Oxide Component	Reagent Used	Frit	Sludge	PHA
Al_2O_3	Al_2O_3	0	16.861	1.200
BaO	$BaCO_3$	0	0.243	0.811
B_2O_3	H_3BO_3	8	0.000	29.305
CaO	$CaCO_3$	0	4.389	0.076
	CaF_2			
Cr_2O_3	$Na_2Cr_2O_7$	0	0.356	0.017
Cs_2O	CsCl	0	0.007	0.995
CuO	CuO	0	0.185	3.801
Fe_2O_3	Fe_2O_3	0	44.123	0.807
K_2O	K_2CO_3	0	0.392	36.918
Li_2O		7	0.000	0.000
MgO	MgO	2	0.354	0.006
MnO_2	MnO_2	0	8.911	0.157
Na_2O	Na_2CO_3	6	12.767	18.462
	$Na_2Cr_2O_7$			
	Na_3PO_4			
	Na_2SO_4			
Nd_2O_3	Nd_2O_3	0	2.148	0.043
NiO	NiO	0	2.647	0.047
P_2O_5	Na_3PO_4	0	0.095	0.028
PbO	PbO	0	0.407	0.007
RuO_2	$RuCl_3$	0	0.097	0.002
SiO_2	SiO_2	77	4.175	0.067
SrO	$SrCO_3$	0	0.096	0.002
TiO_2	TiO_2	0	0.000	7.216
ZnO	ZnO	0	0.308	0.006
ZrO_2	ZrO_2	0	1.407	0.025
Sum of Oxides		100	99.968	99.998
F	CaF_2	0	0.168	0.015
Cl	CsCl	0	1.33	0.058
	$RuCl_3$			
SO_3	Na_2SO_4	0	0.737	0.945

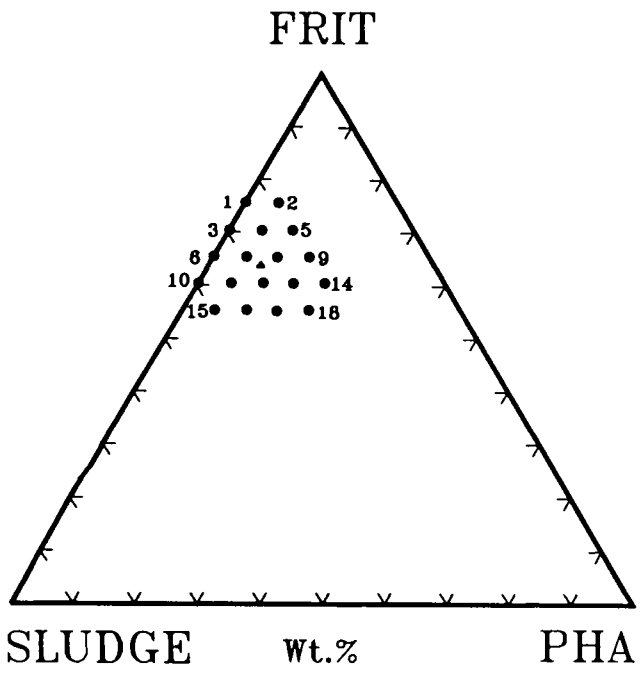

Fig. 1 Triangular diagram showing proportions (by weight) of frit, sludge, and PHA components of samples studied relative to optimum composition, shown by triangle at proportions of frit:sludge:PHA of 64:28:8.

molten glasses the compositions of which are analogous to those used in the radioactive waste disposal process at DWPF.

MATERIALS AND METHODS

Three major components were used for preparing mixtures used in this study: borosilicate glass frit, synthetic sludge, and synthetic PHA. The glass frit was obtained from SRS and is the same material used in the actual waste disposal process. The sludge and PHA were prepared from reagents, using non-radioactive components comparable in chemical behavior to the radioactive elements contained in the actual waste material. The compositions of the materials used and the reagents used in their preparation are given in Table 1. Cationic components are expressed as oxides, i.e., oxygen is listed in stoichiometric proportion to the valence of the cation. Anionic components other than oxygen are listed separately; they are not included in the summation.

All reagents were dried overnight at 115°C before weighing.

Table 3. Measured Shear Stresses for Sample SRL-6 as a Function of Shear Rate and Temperature.

Spindle Speed	Shear Rate	Shear Stress (N/M^2)						
RPM	(1/sec)	1090°C	1110°C	1130°C	1150°C	1170°C	1190°C	1210°C
2	5.9	102.2	87.1					
4	11.7	201.2	163.2	134.7	112.5	104.6	91.1	73.7
6	17.6	294.7	236.1	193.3				
8	23.5	389.8	308.2	251.1	220.2	188.5	162.4	129.1
10	29.3	484.0	381.8	310.5				
12	35.2	578.3	455.5	370.8	325.6	271.7	230.5	186.2
14	41.1	673.4	530.8	433.3				
16	46.9	762.1	605.2	494.3	421.5	363.6	307.4	249.5
18	52.8		675.7	551.4				
20	58.7			606.8	520.5	446.0	381.0	309.0
22	64.5			667.0				
24	70.4				617.9	529.2	452.3	373.1
28	82.1				719.3	605.2	515.7	430.2
32	93.9					690.0	585.4	483.2
36	105.6						655.9	544.2
40	117.3							605.2
44	129.1							663.1

Table 2. Measured Shear Stresses for Sample SRL-2 as a Function of Shear Rate and Temperature.

Spindle Speed	Shear Rate	Shear Stress (N/M^2)						
RPM	(1/sec)	1090°C	1110°C	1130°C	1150°C	1170°C	1190°C	1210°C
1	2.9	42.0	34.1					
3	8.8	127.5	106.9	96.7	80.8			
5	14.7	217.9	178.2	159.2	131.5	114.1	101.4	91.9
7	20.5	308.2	251.1	218.6	183.8	157.6		
9	26.4	396.9	324.8	278.1	235.3	203.6	176.7	155.3
11	32.3	483.2	396.9	337.5	286.0	247.2		
13	38.1	571.2	472.2	392.1	338.3	293.9	251.1	218.6
15	44.0	654.4	544.2	453.1	384.2	333.5		
17	49.9		614.7	517.3	441.3	382.6	328.0	282.0
19	55.7		686.8	573.6	489.6	426.2		
21	61.6			633.0	533.9	467.4	398.5	350.2
23	67.5			692.4	585.4	512.6		
25	73.3				633.8	549.8	471.4	415.9
27	79.2				686.0	594.9		
29	85.1				735.2	634.9	547.4	479.3
31	90.9					678.9		
33	96.8						623.5	541.9
35	102.7							
37	108.5						701.9	603.7

Table 4. Measured Shear Stresses for Sample SRL-9 as a Function of Shear Rate and Temperature.

Spindle Speed	Shear Rate	Shear Stress (N/M^2)						
RPM	(1/sec)	1090°C	1110°C	1130°C	1150°C	1170°C	1190°C	1210°C
5	14.7	68.9						
10	29.3	137.8	115.7	94.3	82.4	76.1		
15	44.0	193.3						
20	58.7	264.6	220.2	186.2	161.6	143.4	124.4	110.1
25	73.3	324.0						
30	105.6	388.2	327.2	284.4	247.2	211.5	183.8	
35	102.7	453.1						
40	117.3	517.3	436.5	376.3	323.2	279.6	241.6	214.7
45	132.0	578.3						
50	146.7	643.3	551.4	461.1	399.3	347.0	308.2	
55	161.3	709.0						
60	176.0	770.0	652.8	553.8	480.9	422.2	371.5	317.7
70	205.3			647.2	560.9	488.0	427.8	
80	234.6			737.5	637.7	556.1	486.4	423.8
90	264.0				714.6	624.3	544.2	
100	293.3					695.6	601.3	530.0
110	322.6						659.9	
120	352.0						721.7	633.8
140	410.6							737.5

Oxide equivalents were calculated for carbonates, phosphates, sulfates, chlorides, and fluorides. Residual water of hydration was measured for H_3BO_3, $Na_2Cr_2O_7$, Na_3PO_4, and $RuCl_3$ using the Penfield method (Penfield, 1894; Potts, 1987); weights were adjusted to account for the hydration. Weighed reagents were combined in powdered form and mixed thoroughly.

Eighteen compositions of synthetic analogs of radioactive wastes were prepared by carefully weighing the appropriate amounts of frit, sludge, and PHA (see Fig. 1). Three of these compositions were selected for preliminary evaluation: samples SRL-2, with proportions of frit:sludge:PHA of 75:20:5; SRL-6, with proportions of 65:35:0; and SRL-9, with proportions of 65:20:15. These samples were chosen to allow evaluation of the effects of changes in the proportions of each of the three components relative to the nominal composition. Each sample was mixed with 15 mL of a 1:10 formic acid solution (one-part acid to ten-parts water) and dried at 110°C until all water evaporated. The dried sample was melted at a temperature of 900°C, then cooled to a glass.

RESULTS AND DISCUSSION

Viscosity was measured using the concentric cylinder technique. The sample was contained inside a $Pt_{80}Rh_{20}$ crucible, with dimensions 25.4-mm ID x 50.8-mm long. A doubly-tapered $Pt_{80}Rh_{20}$ spindle was lowered into the melt and centered with respect to the cylindrical crucible. The overall length of the spindle is 32.9 mm. The cylindrical portion of the spindle is 19.9 mm in length and has a diameter of 14.3 mm. Both ends of the spindle are coned at a 45° angle, and one end is truncated, drilled and tapped to accommodate a 2.4-mm diameter stem, which connects the spindle to a Brookfield RVDV-III rheometer. The rheometer is under computer control. This assembly was calibrated at room temperature using manufacturer supplied silicone-based viscosity standards of 30 Pa . sec (300 poise) and 60 Pa . sec (600 poise) and at high temperature (approximately 1235°C) using National Institute of Standards and Technology Standard Reference Material 711, a lead silicate glass.

Viscosity measurements were taken at seven different tempera-

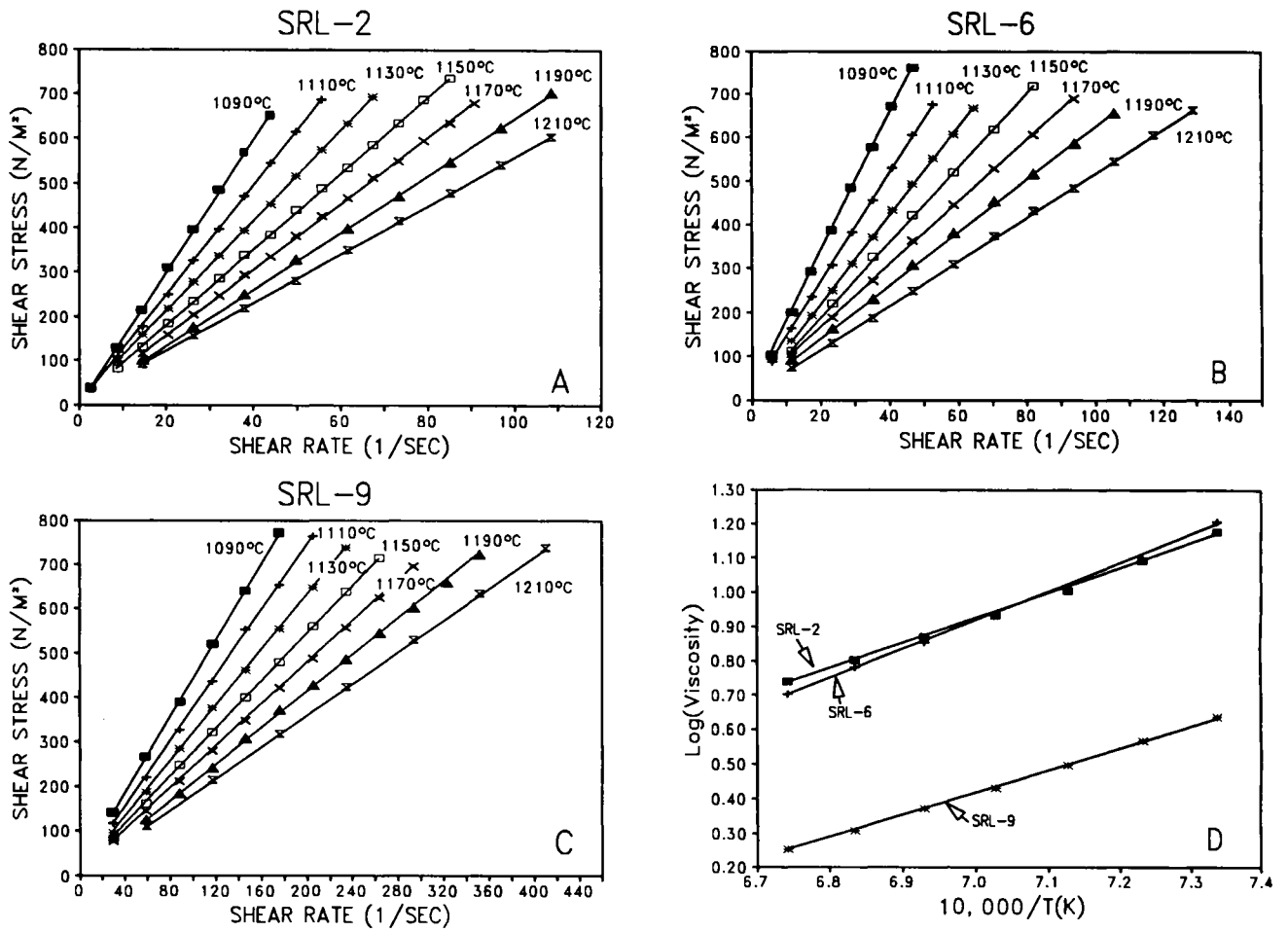

Fig. 2. Temperature effects on rheology of the three samples studied. A-C, measured shear stress vs. shear rate for samples SRL-2, SRL-6, and SRL-9, respectively. The slope of the line at each temperature yields the viscosity coefficient in Pa-sec. D, Arrhenius plot of log(viscosity coefficient) vs. reciprocal temperature (Kelvin) for the three compositions studied.

tures, from 1090°C to 1210°C in increments of 20°C, for each composition studied. The crucible containing the sample was placed in a vertical-tube furnace and the temperature slowly raised to 1090°C. Angular velocity (RPM) of the spindle was adjusted to a value yielding between approximately 5-10% toque, as measured by the rheometer. The spindle was allowed to rotate at this speed for a minimum of one hour to homogenize the sample and encourage the liberation of trapped air bubbles. The value for the percentage torque decreased during the first 15 to 30 minutes at constant temperature and spindle speed. Data were not taken until a constant torque value was recorded for at least 30 minutes.

Measurements were taken at several different spindle speeds, specified to span the range from approximately 10% to 90% torque, for each temperature investigated. Data were automatically recorded by computer following pre-set time intervals of sufficient duration to allow the spindle to complete a minimum of 10 revolutions (twice that recommended by the rheometer manufacturer) between readings. Spindle speed and percent torque were converted to shear rate (1/sec) and shear stress (N/M^2), respectively, based on the calibration determination described above. Data are presented in Tables 2-4 and shown graphically in Fig. 2.

Viscosities were calculated from these data using a linear regression for shear stress divided by shear rate. These calculated values are presented in Table 5. Confidence of fit for each data set is 99% or better. All samples were found to be Newtonian liquids, i.e., having linear relationships between shear stress and shear rate with a yield stress of approximately zero. An Arrhenius plot of log(viscosity) vs. reciprocal temperature for all samples is shown in Fig. 2D; these data exhibit a linear relationship for each composition over the temperature range investigated. Figure 3 is an isothermal diagram showing the change in viscosity with composition. These data show that viscosity increases with frit content and decreases with PHA content. Preliminary evaluation of the data, assuming linear interpolation of isoviscosity lines between the compositions studied, yields the empirical equation

viscosity = (0.155 x wt% frit) – (0.044 x wt% sludge) – (0.445 x wt% PHA) (1).

This equation yields a value of 5.1 Pa · sec for the viscosity for the target composition, compared to the reported value of 4.9 Pa · sec (Ray Schumacher, Savannah River Laboratory, personal communication, 1992). We thus conclude that changes in viscosity can be treated as linear functions of composition for the compositional range studied. These results support the argument of Schneider (1990) that viscosity can be used as an indicator of composition, even for relatively complex mixtures. However, the empirical equation determined above is valid only for the particular mix of components used at SRS; other high-level radioactive waste disposal operations for which the products of waste processing differ significantly from those at SRS will be required to evaluate the compositional effects of viscosity unique to their particular facility.

Future work will center on determination of changes in melt density as a function of composition at the process temperature. These data will be combined with the viscosity data to provide a method to uniquely identify melt compositions, using physical property measurements. Long term goals include developing generally applicable equations for viscosity changes over a very wide compositional range relevant to vitrification of high-level radioactive waste. For example, Bottinga and Weill (1972) formulated a model for calculating viscosities of naturally occurring rock compositions in the molten state for a relatively wide range of SiO_2 contents. Ideally, similar empirical equations will be determined for the much more complex and arbitrary compositions encountered in the disposal of nuclear wastes.

Table 5. Viscosities (Pa·sec for Three Samples Studied Calculated as Shear Stress/Shear Rate.

Temperature	Viscosity (Pa·sec)		
(°C)	SRL-2	SRL-6	SRL-9
1090	15.00	16.08	4.34
1110	12.39	12.55	3.69
1130	10.12	10.13	3.13
1150	8.56	8.56	2.70
1170	7.41	7.14	2.35
1190	6.36	6.03	2.03
1210	5.49	5.05	1.79

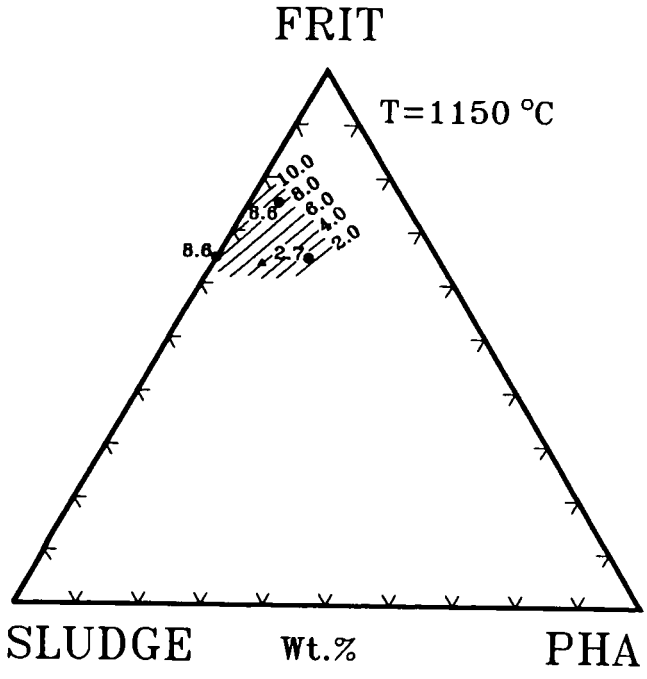

Fig. 3. Variation of viscosity as a function of composition at 1150°C. Bold numerals are measured values. Italicized numerals correspond to isoviscosity contours, calculated using equation (1). Optimum composition, represented by triangle, has reported viscosity of 4.9 Pa·sec (see text).

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